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(54) Bioactive coating and fixing composition for plant protection

(57) A bioactive coating composition for plant protection and seed germination contains a water-soluble protein of natural origin and a salt or complex of Zn, Mg, Mn, Fe, Co, Cu and Mo which together form a hydrophilic, water-insoluble coating.

The composition may also contain, a dye, a surfactant, a pesticide or a fertilizer. The protein binding agent is preferably casein, albumin, collagen, keratin, soya protein or wheat gluten and provides biologically degradable decomposition products harmless to the environment.

The composition is not freeze-sensitive and can be stored in a vessel for years and diluted with water unrestrictedly.

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SPECIFICATION

Bioactive coating and fixing composition for plant protection

The invention relates to a bioactive coating and fixing composition generally usable in the agriculture. Said composition contains at least one reversibly water-soluble protein of natural origin, furthermore at least one non-phyto-toxic salt or complex of Zn, Mg, Co, Fe, Mn, Cu, Ti and Mo, optionally plant protection agents known *per se* and usual auxiliary agents. The composition of the invention exerts — in comparison to similar products used up to now — a bioactive effect. Its aqueous solution forms, after drying, a water-insoluble film which, due to its structure, accelerates and intensifies the germination of seeds. The composition of the invention sprayed on leaves enhances the biological processes of the plants and in certain cases it prolongs the effect of the plant protection agents. The binding agent of the composition of the invention provides biologically decomposable decomposition products harmless to the environment, thus it possesses an environment-preserving effect.

Chemical plant protection plays a determining role in the agricultural production nowadays. Phytopathogenic fungi and harmful insects can destroy 30—50% of the potential harvent. In order to minimize these losses chemicals are widely used.

The protection of the plants can be carried out by seed treatment or postemergence spraying.

The chemicals used for seed dressing are generally applied to the seeds by dusting or wet dressing. The chemicals applied in that way do not stick reliably and their distribution cannot be controlled, wherefore the effect is uncertain. The protective coatings sprayed on the plants are not water-resistant, thus the rain easily washes off said coatings.

Due to the above reasons the plant protection agents are used in a manyfold excess in the case of both types of the seed dressing. Besides the cost factors this represents danger toward the environment and human beings.

In order to eliminate said deficiencies in the developed industrial countries varnish-paint coatings were used for seed dressing (see e.g. the US patent specification No. 3,113,339) already in the sixties.

The cited patent specification describes varnishes and dispersions based on synthetic resins among which the varnishes containing a synthetic resin and solvent therefor are not phytotoxic only on a rather limited territory and between limited parameters. From time to time they are inflammable and can explode and the solvents thereof are more or less toxic. The varnish coatings according to said patent are biologically not decomposable and their compatibility with the active ingredients of the plant protection agent is limited.

The storage stability of the products according to the cited patent is very limited and when cooled below the freezing point and/or optionally on the effect of a plant protection agent they coagulate irreversibly and thus become unfit for use. The binding agents of the synthetic dispersions are also not decomposable biologically.

The general disadvantage of the synthetic film seed dressing resides in the fact that the synthetic resin film, which is generally known to be water-tight, hinders and retards the water absorption and thus the germination of the seeds, especially in dry soil; further, it causes significant plant loss if there is a cold period in the course of the emergence.

In the course of our tests we believe we succeeded in the elaboration of film forming coating systems which possess fewer, if any, of the deficiencies of the above known solutions and which even exert completely novel effects in comparison with the known ones.

The invention is based on the recognition that reversibly water-soluble animal and plant proteins of natural origin, e.g. casein, albumin, collagen, hydrolyzed keratin, soya protein, wheat gluten, provide in combination with appropriate metal compounds mixtures from the solution of which a water-insoluble, but sufficiently hydrophilic bioactive coating is formed by drying. Such coatings exert, surprisingly, a germination-promoting and growth-increasing effect too, in addition to the effect of the plant protecting agents embedded into them asserting itself without any restriction.

The invention relates to a bioactive coating and fixing composition for plant protection characterized by containing at least one reversibly water-soluble protein of natural origin and at least one compound selected from the group of the salts and complexes of Zn, Mg, Mn, Fe, Co, Cu and Mo together with usual additives and optionally a plant protecting agent or a plant protecting composition.

The most important raw materials of the composition according to the invention are easily accessible and of agricultural origin. Neither the basic materials nor the final products are toxic in the course of the production and the use and they decompose biologically rapidly to nutrient materials which can be used by the plant.

The composition of the invention is not freeze-sensitive, in a closed vessel it can be stored for years and it can be diluted with water unrestrictedly. It wets the surface of the seeds rapidly and completely and forms a well-adhering, equal, hard, flexible and water-insoluble coating on it. When using it as an additive for spray liquors it ensures the optimal distribution and the rain-proof adherence of the plant protection agent on the surface of the plant.

The composition of the invention exerts a bioactive effect since our tests carried out over an extended period have proved that besides the adhering and protecting effect it promotes the germination and growth of the seeds. When added to any kind of a spray liquor it increases the rainproofness of the coatings significantly and

moreover, it promotes the growth of the plants and increases their resistance against diseases caused by fungi.

The composition of the invention contains a protein suitably in an amount of 10 to 99 percent by weight, while a metal compound in an amount of 0.05 to 5 percent by weight.

In the course of the selection of the metal salts and metal complexes, respectively, used for the production of the complexes of the invention different metal compounds, e.g. inorganic and organic salts, furthermore complexes prepared with usual chelating agents, e.g. ethylenediamine tetraacetic acid, and mixtures thereof, respectively, can be used. The water-solubility of the compounds used is not of determining importance, e.g. water-insoluble zinc phosphate or another inorganic, water-insoluble metal salt can be used if it is ground to a sufficiently fine size, suitably to a particle size of smaller than 20 micron. For the use of seed dressing compounds of Zn, Mg and Mn proved to be specially good, in the case of a composition applied on the leaves of the plants in the vegetation period besides Zn, Ti and the usual trace elements of the spray dressings, e.g. Fe, Cu, Co and Mo, are additives of good effect.

The composition of the invention can be prepared e.g. in form of a solution or a suspension, respectively, and in the practice these are the most suitable formulations. The composition of the invention can, similarly to the powdery paints based on dry casein, also be prepared in powdery form, and from this form the desired solution of suspension, respectively, can be prepared at the place of use, e.g. in the field.

If from the compositions of the invention a pesticide, e.g. a fungicide, insecticide, acaricide and/or nematocide, is to be prepared, active ingredients ensuring the desired protective effect must be added in an effective amount. The corresponding active agents can be added in a sufficiently fine ground form. However, one can also proceed so that a plant protection composition ready for use is added to the composition of the invention.

As fungicides for example dithiocarbamates or thiuram derivatives, e.g. zinc-ethylene-bis-dithiocarbamate, manganese-ethylene-bis-dithiocarbamate, tetramethyl-thiuram-disulfide; phthalimide derivatives, e.g. N-trichloro-methyl-mercapto-4-cyclohexene-1,2-dicarboximide (Captane), N-trichloromethyl-mercapto-phthalimide; nitrobenzene derivatives, e.g. tetrachlorodinitrobenzene, pentachloro-nitrobenzene; systemic fungicides, e.g. 8-oxyquinoline-copper(II) complex (copperoxyquinolate), 1-[(butylamino)-carbonyl]-1H-benzimidazole-2-yl-carbamate (Benomyl), 5,6-dihydro-2-methyl-N-phenyl-1,4-oxathiin-3-carboxamide (Carboxine), etc. can be used. As insecticides for example chlorinated hydrocarbons can be used, e.g. Methoxychlor, DDT and so on; further, organic phosphoric acid esters, e.g. DDVP, Malathion, Parathion, Diazinon; and carbamate derivatives, e.g. Carbaryl, Carbofurane.

In order to regulate the film-forming properties of the composition of the invention, different auxiliary agents can be used. The flexibility of the film layer is regulated by auxiliary agents of softening effect, e.g. by oils of mineral or plant origin; di- and polyhydroxy alcohols, e.g. glycol, polyglycol or glycerine; optionally partial esters of polyols, e.g. trimethylolpropane capronic acid ester, dodecylcarboxylic acid monoglyceride, and so on; or partial esters of di- and polycarboxylic acids, e.g. monooctyl phthalate, monobutyl phthalate or the salts thereof, e.g. ammonium salts thereof which act as surfactants besides their softening effect.

In order to regulate the distribution, the adherence and the permeability of the films formed by the compositions of the invention, surface active agents can be used, too. As surface active agents anion-active and non-ionic ones can be used according to the desired film properties. Surfactant of these types are described e.g. on pages 199—285 of the book "Chemical Technology" of Winacker-Kühler (issued by Technical Editory, Budapest, 1963).

As preservative materials of the compositions of the invention mould-inhibiting additives can be used, e.g. sodium pentachlorophenolate, sodium benzoate or sodium salicylate.

When the composition of the invention is used in seed dressing water-soluble basic dyestuffs can be used in order to distinguish the dressed seeds. Thus e.g. rhodamine dyestuffs, nigrosine base, water-soluble indulines and so on can be used.

The invention is illustrated with the aid of the following examples without restricting the present invention to these examples.

EXAMPLE 1

Into a mixing reactor, prepared from stainless steel, with steam heating 80 kg of deionized water are weighed and heated to 60°C. Under stirring 10 kg of pulverized acid casein are added. In 4 l of a 25 vol. % aqueous ammonia solution 65 g of zinc phosphate are dissolved. The solution is added to the casein suspension in a thin jet. After the addition the mixture is stirred for 1 hour. A slightly opalescent solution is obtained. Then 600 g of a non-ionic emulsifier (Emulsogen 10 of Hoechst) and 500 g of polyglycol (Lanogen 1500 of Hoechst) and 35 g of sodium pentachlorophenolate are added to the solution. Finally 12 g of Rhodamine B dyestuff are added to the solution and the mixture is stirred until it fully goes into solution.

EXAMPLE 2

One proceeds as in Example 1 but instead of casein soya protein is used and 0.1 part by weight of a 26° Baumé aqueous ammonia solution is added based on 1 part by weight of soya protein.

EXAMPLE 3

90 kg of deionized water are filled into a heated reactor provided with a mixer and under steady

stirring 15 kg of bone glue are added. The heating of the reaction mixture is begun and, when 80°C are reached, 1 kg of ethylene-diamine-tetraacetic acid titane complex and 4 g of ethylene-diamine tetraacetic acid magnesium complex are added to the reaction mixture. After half an hour 0.8 kg of ethoxylated nonylphenol (containing 10 mole of ethyleneoxide), 1 kg of propyleneglycol, 0.2 kg of benzenesulfochloroamidesodium and 0.005 kg of Ostazin Brillantrot H 3B dyestuff are added. After cooling 20 kg of 1-[(butylamino)-carbonyl]-1H-benzimidazole-2-yl-carbamate as a fungicide are admixed into the mixture and the latter is reduced to an average particle size of 2 nm in a pearl mill. The product of the example can be used for seed dressing.

EXAMPLE 4

Into an autoclave provided with a mixer 80 kg of water are weighed and under continuous stirring 20 kg of blood albumen are dispersed into it. At room temperature (20—25°C) the mixture is stirred until dissolution. Then 0.8 kg of mangesium ammoniumphosphate and 0.1 kg of ethylene-diaminetetraacetic acid molybdenum complex are added to the mixture. After half an hour of stirring still 1 kg of sodium lauryl sulfate, 0.2 kg of toluenesulfonamide-chlorosodium, 5 kg of urea and 0.008 kg of Rhodamine G dyestuff are added. The product is thoroughly admixed with 15 kg of Captane (N-trichloro-methyl-mercapto-4-cyclohexene-1,2-dicarboximide). The product of the example can be used for seed dressing.

EXAMPLE 5

To 8 parts by weight of the solution of Example 1 2 parts by weight of Orthocid 50 WP are admixed. Without any dilution the obtained suspension can be used for the dressing of seeds. If the suspension is diluted with soft water to a hundred-fold, it can be used as a fungicide for spraying.

The Orthocid 50 WP suspension diluted according to the example was sprayed on glass plates and dried, then 10 mm of artificial rain was caused to fall on it. After the rain 87% of the spray coating remained unchanged on the glass plates.

The parallel coating but without the composition of the invention was practically completely washed away from the surface by the 10 mm of rain.

With the Orthocid suspension diluted according to the example spraying was carried out every other week in a peachery of type Elberta. As control parallel aqueous Orthocid suspension without the composition of the invention was sprayed onto the trees in a concentration of similarly 0.1%.

The product of the example provides complete protection against leaf-crisping (Taphrina) and on the effect of the composition of the invention the crop was significantly more colourful than the control. In the control parcel the infection gradually developed and at the end of the vegetation period it reached 35—38%.

EXAMPLE 6

9 parts by weight of the product of Example 2 based on soya protein are admixed with 1 part by weight of TMTD (tetramethyl-thiuram-disulfide) with an average corn size of 100 nm in a homogenizer until the mixture becomes homogeneous. The obtained mixture is preground in a corundum disc mill to a particle size of 20 nm, then it is ground to an average particle size of 2 nm in a pearl mill of the system Netsch. The product of the example can be used for the dressing of maize seeds.

Maize seeds were dressed with the product of the example [200 g of TMTD active agent/q seed]. As a control seed dusting was carried out in the same dose.

The maize dressed by the product according to the invention remained free of infection with nigrospore and fusarium. From 100 sown seeds 98 emerged. The coming up seedlings were of bright green colour and, in relation to the control, they showed a difference in height of 26—29%. The emergence percentage of the control was 76 because of the fungi infection.

EXAMPLE 7

15 kg of fine-ground casein powder, 1000 g of dodecylbenzenesulfonate, 200 g of $Zn_3/PO_4/_2$, 200 g of Chloramine T and 5 g of Rhodamine G dyestuff are filled into a ball mill and homogenized. The thus-obtained powder is transported to the place of use. At the site 95 l of water with a temperature of 50—60°C are admixed with 6 kg of a 25 percent aqueous ammonia solution and under continuous stirring the powder is poured into it. After dissolution 18 kg of Quinolate V4X are admixed into it so that it is completely free of lumps. The product can be used for seed dressing.

EXAMPLE 8

To 90 parts by weight of softened water 4 parts by weight of the binding agent according to Example 1 are added, then under continuous stirring 3 parts by weight of colloidal sulphur composition [880 g of sulphur/l] and 2 parts by weight of dinitro-o-cresol ammonium salt (containing 25% a.i.), which previously was diluted with the same quantity of water of a temperature of 80°C, are added, finally 0.01 part by weight of NONIT (sodiumdioctylfosuccinate) wetting agent is added to the mixture. With the obtained spray liquid winter spraying is carried out by using 10 l of the spray liquid per bearer unit. After drying the thus-obtained coating is rain-proof and it protects the trees against fungal infection in the spring vegetation period.

EXAMPLE 9

1.2 kg of the composition of Example 1 are thoroughly mixed with 100 g of Orthocid 50 WP and 100 g of Quinolate V4X. 100 g of water are added and the mixture is homogenized thoroughly. The thus-prepared dressing material is added to 100 kg of sugar-beet seeds and in a rotary mixer it

is applied to the surface of the seeds in a uniform layer. Then 3 kg of bentonite are added and under further stirring and rotating it is adhered onto the surface of the dressed seeds. The seeds become round and bigger, thus they can be sown seed by seed.

EXAMPLE 10

4 l of the leaf-fertilizer product Wuxal® are dissolved in 80 l of water, then 2.5 kg of the composition of Example 1 are added so that the latter is previously diluted gradually with 1 l of water under continuous stirring. The thus-prepared spray is sprayed onto 1 hectare of an apple-orchard as leaf-fertilizer by aeroplane.

EXAMPLE 11

5 kg of the leaf-fertilizer product Peretrix® are dissolved in 400 l of water, 12 kg of the composition of Example 2 diluted with 3 l of water are added and after thorough mixing it is sprayed onto 1 hectare of peachery by a spraying machine.

In order to prove the effect of the compositions according to the invention *in vitro* and *in vivo* examinations were carried out.

In the *in vitro* trials maize germination tests were carried out as follows.

Hybrid maize seed MV-27 was germinated in a Petri-dish. In the tests undressed seed, the bioactive product according to example 1 of the invention and the seeds dressed with the film former (free of a.i.) of the US patent No. 3,113,339 were used. The germination was carried out at a temperature of 20°C for 8 days in identical soil under identical conditions. After 8 days the length of the germinated maize root and stem was measured.

The average radicle length of the maize dressed by said film former was 2 mm, the average radicle length of the undressed seeds 6 mm, while the radicles of the seeds dressed with the composition of the invention were generally 9 mm long, thus the latter increased the germinating powder by 50%, based on the untreated seeds.

In field experiments peas, beans and maize were dressed with the composition of Example 6 by using 8 l of the product for 100 kg of seeds. As control undressed seeds and such seeds were used which were dressed with the binding agent of the US patent specification No. 3,113,339.

The height of the seedlings was measured after 3 weeks. 20—30% of the undressed seeds were destroyed, while the plants emerging from the seeds dressed with said binding agent were generally 30% smaller than those emerging from the seeds treated with the compositions according to the invention.

CLAIMS

1. A bioactive coating and fixing composition for plant protection, comprising at least one reversibly water-soluble protein of natural origin and at least one salt or complex of Zn, Mg, Mn, Fe, Co, Cu or Mo together with usual additives and optionally a plant protecting agent or a plant protecting composition.

2. A composition as claimed in claim 1, wherein said protein is present in an amount of 10 to 99 percent by weight and said metal compound is present in an amount of 0.05 to 5 percent by weight.

3. A composition as claimed in claim 1 or 2, wherein as said reversibly soluble protein casein, albumen, collagen, hydrolyzed keratin, soya protein or wheat gluten is used.

4. A composition as claimed in any preceding claim, wherein as softener a polyol or a partial ester of a polyol and/or a partial ester of a di- or polycarboxylic acid, e.g. in a quantity of 0.1 to 10% by weight is used.

5. A composition as claimed in any preceding claim, wherein said composition further contains an anionic and/or non-ionic surfactant e.g. in a quantity of 0.1 to 5% by weight, as a preservative at least one material of fungicidal effect, e.g. in a quantity of 0.01 to 1% by weight, and optionally as a dyestuff at least one water-soluble basic dyestuff, e.g. in a quantity of 0.001 to 5% by weight.

6. A composition as claimed in any preceding claim, further containing an insecticidal or fungicidal substance, e.g. in a quantity of at most 30% by weight, as additive.

7. A composition according to claim 1 substantially as herein described in any one of the Examples.

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